

Thermodynamics of complex formation of Ag(I). Part VIII. Investigations on Ag(I)–thiourea–thiocyanate– halide systems in aqueous solution

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(Received 26 April 1991)

Abstract

Complex formation in the three-ligand systems Ag(I)–SCN₂H₄–SCN[–]–X (X = Cl[–], Br[–], I[–]) has been investigated by potentiometry in aqueous solution at ionic strength $\mu = 1$ using KNO₃ and different temperatures.

Enthalpy and entropy changes have been evaluated from the free energy change dependence on temperature.

Predominance diagrams for the two-ligand systems Ag(I)–SCN[–]–X (X = Cl[–], Br[–], I[–]) and the three-ligand systems Ag(I)–SCN₂H₄–X (X = Cl[–], Br[–], I[–]) at 25 °C and $\mu = 1$ for KNO₃ are shown.

The free energy changes for the coordination reactions of thiourea or thiocyanate indicate higher affinities for the dicoordinated substrata than for the monocoordinated ones.

The ionic charges of both the substrata and the entering group are not the main factors in determining the affinity sequences.

The parameters of the Gibbs equation are interrelated, though in different ways, in both the overall and stepwise complex formation.

LIST OF SYMBOLS

Tu	thiourea
Tcy	thiocyanate ion
Ts	thiosulphate ion

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L, X, Y, Z	ligands
Sub	Ag(I) complex substratum
ΔG , ΔH , ΔS	free energy, enthalpy and entropy changes (kJ mol^{-1} , kJ mol^{-1} , $\text{kJ mol}^{-1} \text{K}^{-1}$) for the overall coordination reactions $\text{Ag(I)} + m\text{X} + n\text{Y} + \dots = \text{Ag X}_m\text{Y}_n\dots$
$\Delta \bar{G}$, $\Delta \bar{H}$, $\Delta \bar{S}$	free energy, enthalpy and entropy changes (kJ mol^{-1} , kJ mol^{-1} , $\text{kJ mol}^{-1} \text{K}^{-1}$) for the stepwise coordination reactions $\text{Sub} + \text{X} = \text{Sub X}$
β_i	stability constant for the overall coordination reaction $\text{Ag(I)} + m\text{X} + n\text{Y} + \dots = \text{AgX}_m\text{Y}_n\dots$ ($\text{mol}^{-i} \text{dm}^{3i}$) ($i = m + n + \dots$)
K	stability constant for the stepwise (single ligand) coordination reactions ($\text{mol}^{-1} \text{dm}^3$)
$\log X$ or $\lg X$	$\log_{10} X$
$[\text{X}]_{\text{tot}}$	total analytical concentration of X
$[\text{X}]_{\text{free}}$	free (solvated) concentration of X
N_{max}	maximum coordination number
In some cases, charges are omitted for simplicity.	

INTRODUCTION

In solutions containing one or more suitable ligands and one or more suitable acceptors, mixed complexes are always formed. In systems with one metal ion M and two different donors (X and Y), mixed ligand complexes occur together with single ligand complexes, MX_n and MY_m on condition that $[\text{X}] > 0$ and $[\text{Y}] > 0$ and that the maximum coordination number of the acceptor is greater than 1 ($N_{\text{max}} > 1$).

The occurrence of at least two coordination sites on the central ion is a necessary condition for the formation of mixed complexes and, in general, n coordination sites are needed for the occurrence of n different mixed ligand complexes. Because the condition $N_{\text{max}} > 1$ is met by all metal ions, their solutions with more ligands always contain mixed complexes.

However, the quantitative aspects of the system are strictly related to the characteristics of the system itself (the number and types of the complexes, the stability constants, the analytical concentration of the independent species) and reflect the occurrence of stabilisation (destabilisation) factors for the simultaneous presence of different ligands in the coordination sphere. In general, the predominance of the various complexes depends on the complexing ability of the system.

By changing systematically only one of the ligands in the system, complexes with the same acceptor, but systematically different in one ligand are obtained. In this way the chemical environment of the central ion is modified and its influence on coordination and/or displacement reactions with the same acceptor can be investigated.

From previous investigations on Ag(I)-Tu-Ts-X ($X = \text{SCN}^-$, Cl^- , Br^- , I^-) [1] and Ag(I)-Tu- SCN^- - NH_3 [2] systems in aqueous solution, the following conclusions can be derived.

(i) The affinity ($-\Delta\bar{G}$) sequences of Ag(I) complex substrata for the coordination reaction $\text{Sub} + \text{L} = \text{Sub-L}$ (Sub = Ag(I) complex substratum) remain unaltered, independent of the nature and ionic charge of the incoming ligand L. The sequences are also unchanged for displacement reactions $\text{Sub-X} + \text{L} = \text{Sub-L} + \text{X}$.

(ii) Ion complexes with charges opposite in sign occur, in contiguous positions in the above-mentioned sequences, i.e. the pairs $\text{AgTu}^+ - \text{AgTs}^-$ or $\text{AgTsBr}^{2-} - \text{AgTu}^+$.

(iii) No regularity is found between the sequences of substrata and their formal ionic charges.

These remarks lead to the conclusion that the ionic charges of both the substratum and/or the incoming or leaving ligand are not the main factors in determining the association between Ag(I) and the investigated ligands in aqueous solution.

Moreover, it has been demonstrated that exponential relationships ($Y = A + B \exp(-CX)$) occur between the affinities of Ag(I) substrata toward incoming ligands ($Y = -\Delta G$) and their overall stabilities with respect to the reagents ($X = -\Delta G$). The data already published show some gaps which must be filled to obtain reliable quantitative definitions of the parameters A , B and C of the above-mentioned relationship.

By replacing $\text{S}_2\text{O}_3^{2-}$ with SCN^- in the system, Ag(I) complex substrata are obtained with lower thermodynamic stabilities and more positive formal charges, but with the same donor atom as the parent complexes with thiosulphate. (Parent complexes are complexes having the same number of coordinated ligands but having at least one ligand different.) The results of the present research are useful for corroborating previous hypothesis concerning both the role of the ionic charges of the substrata and the exponential dependence of the mutual substratum-to-ligand chemical affinities on the overall thermodynamic stabilities of the reacting substrata.

EXPERIMENTAL

The systems investigated were Ag(I)-thiourea-thiocyanate-chloride; Ag(I)-thiourea-thiocyanate-bromide; Ag(I)-thiourea-thiocyanate-iodide.

Reagents

AgNO_3 , NaSCN , KCl , KBr and KI were employed for preparing the respective solutions. They were standardised in the classical way.

TABLE 1
 $\text{Log } \beta_n \text{ (mol}^{-n} \text{ dm}^{3n})$ for the overall complex formation $\text{Ag(I)-SCN}_2\text{H}_4\text{-SCN-X}$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$) in aqueous solution and ionic strength $\mu = 1$ for KNO_3 at different temperatures

Formula	S	0 °C	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C
AgTu ⁺	Cl ⁻	-	7.63 ± 0.1	-	6.98 ± 0.08	-	7.37 ± 0.2	6.75 ± 0	-	6.49 ± 0.2
	Br ⁻	8.28 ± 0.14	-	8.55 ± 0.1	-	6.58 ± 0.04	5.75 ± 0.2	-	7.98 ± 0.2	-
	I ⁻	-	-	-	5.76 ± 0.04	-	6.01 ± 0.1	-	6.36 ± 0.1	5.92 ± 0.07
AgTu ₂ ⁺	Cl ⁻	-	11.38 ± 0.1	-	11.03 ± 0.05	-	-	-	-	-
	Br ⁻	12.24 ± 0.04	-	9.82 ± 1.2	-	9.98 ± 0.11	9.24 ± 0.3	-	-	-
	I ⁻	-	-	-	10.34 ± 0.09	-	10.12 ± 0.1	-	9.64 ± 0	-
AgTcy	Cl ⁻	-	6.60 ± 0.1	-	5.43 ± 0.08	-	4.85 ± 0.4	4.63 ± 0.05	-	-
	Br ⁻	7.07 ± 0.08	-	6.44 ± 0.04	-	4.68 ± 0.04	4.36 ± 0.19	-	6.04 ± 0.12	-
	I ⁻	-	-	-	5.59 ± 0.11	-	3.97 ± 0.22	-	4.87 ± 0.12	4.53 ± 0.08
AgTcy ₂ ⁻	Cl ⁻	-	6.94 ± 0.8	-	7.73 ± 0.3	-	6.53 ± 0.6	7.14 ± 0.5	-	7.43 ± 0.05
	Br ⁻	8.69 ± 0.04	-	8.6 ± 0.05	-	6.89 ± 0.04	6.96 ± 0.03	-	8.05 ± 0.09	-
	I ⁻	-	-	-	5.9 ± 0.22	-	5.50 ± 0.12	-	6.27 ± 0.15	6.10 ± 0.09
AgTuTcy	Cl ⁻	-	9.85 ± 2	-	9.45 ± 0.05	-	9.51 ± 0.18	8.99 ± 0.2	-	8.29 ± 0.1
	Br ⁻	10. ± 0.21	-	10.6 ± 0.04	-	8.18 ± 0.08	7.69 ± 0.22	-	9.65 ± 0.14	-
	I ⁻	-	-	-	8.46 ± 0.13	-	7.74 ± 0.13	-	7.85 ± 0.26	7.9 ± 0.09

AgTuTcy ₂	Cl ⁻	-	11.21 ± 0.2	11.31 ± 0.08	-	-	10.67 ± 0.3	11.02 ± 0.1	-	-
	Br ⁻	12.32 ± 0.03	-	12.10 ± 0.	10.09 ± 0.35	10.20 ± 0.09	10.09 ± 0.35	-	10.8 ± 1	-
	I ⁻	-	-	-	10.72 ± 0.09	-	10.35 ± 0.16	-	10.49 ± 0.03	10.0 ± 0.03
AgTu ₂ Tcy	Cl ⁻	-	13.88 ± 0.3	-	13.21 ± 0.08	-	-	-	-	-
	Br ⁻	13.96 ± 0.02	-	-	-	11.72 ± 0.09	-	-	-	-
	I ⁻	-	-	-	-	12.00 ± 0.09	-	-	-	-
AgCl	Cl ⁻	-	4.99 ± 0.1	-	4.4 ± 0.05	-	4.46 ± 0.2	3.97 ± 0.08	-	3.93 ± 0.1
AgTuCl	Cl ⁻	-	8.47 ± 0.02	-	8.21 ± 0.1	-	8.34 ± 0.7	7.65 ± 0.08	-	7.70 ± 0.2
AgTcyCl ⁻	Cl ⁻	-	6.76 ± 1.2	-	6.83 ± 0.08	-	5.55 ± 2	6.13 ± 0.05	-	5.59 ± 0.3
AgTuTcyCl ⁻	Cl ⁻	-	11.36 ± 0.2	-	9.85 ± 0.3	-	10.37 ± 0.6	10.12 ± 0.3	-	9.96 ± 0.08
AgTcy ₂ Cl ²⁻	Cl ⁻	-	8.65 ± 0.6	-	8.82 ± 0.5	-	9.11 ± 0.3	8.87 ± 0.3	-	-
AgBr	Br ⁻	6.58 ± 0.04	-	6.63 ± 0.12	-	5.55 ± 0.03	5.11 ± 0.09	-	6.2 ± 0.7	-
AgTuBr	Br ⁻	9.78 ± 0.17	-	10.32 ± 0.11	-	8.45 ± 0.03	7.54 ± 0.03	-	9.59 ± 0.09	-
AgTcyBr ⁻	Br ⁻	8.67 ± 0.16	-	8.11 ± 0.16	-	6.32 ± 0.08	5.76 ± 0.09	-	7.96 ± 0.08	-
AgTuTcyBr ⁻	Br ⁻	12.13 ± 0.4	-	11.99 ± 0.11	-	9.97 ± 0.21	9.72 ± 0.6	-	11.71 ± 0.26	-
AgTcy ₂ Br ²⁻	Br ⁻	10.03 ± 0.09	-	10.16 ± 0.34	-	8.41 ± 0.29	8.26 ± 0.08	-	9.72 ± 0.21	-
AgI	I ⁻	-	-	-	7.22 ± 0.1	-	8.68 ± 0.06	-	8.14 ± 0.08	7.65 ± 0.05
AgI ₂	I ⁻	-	-	-	13.55 ± 0.09	-	13.07 ± 0.26	-	12.79 ± 0.11	-
AgTul	I ⁻	-	-	-	11.54 ± 0.04	-	11.91 ± 0.09	-	11.61 ± 0.1	11.06 ± 0.26
AgTcyI ⁻	I ⁻	-	-	-	10.37 ± 0.18	-	10.08 ± 0.18	-	9.79 ± 0.1	9.15 ± 0.2
AgTcyTul ⁻	I ⁻	-	-	-	13.50 ± 0.39	-	13.14 ± 0.51	-	13.49 ± 0.2	12.51 ± 0.3
AgTcy ₂ I ²⁻	I ⁻	-	-	-	12.11 ± 0.43	-	11.76 ± 0.11	-	10.73 ± 0.87	11.72 ± 0.3

The ionic strength μ in both titrand and titrant solutions was adjusted to 1 using KNO_3 , such that it remained constant in the titration cell during the titrations.

Measurements

The study was carried out by potentiometry using a silver wire as the measuring electrode, coupled to a saturated calomel electrode via a KNO_3 saturated salt bridge. Potentials were measured by an Amel mod. 355 apparatus.

Silver nitrate solutions containing thiourea NaSCN and KNO_3 up to $\mu = 1$, were titrated with potassium halide solutions in a thermostatted room (see Table 1 for the temperatures). Stable, colourless Ag(I) -thiourea solutions can be prepared by adding Ag(I) solution with continuous stirring to a neutral or slightly acidic solution containing excess thiourea. On adding Tu to Ag(I) solutions or when $[\text{Ag(I)}]_{\text{tot}} \approx [\text{Tu}]_{\text{tot}}$, unstable solutions, white precipitates and, finally, black products are obtained. Therefore, excess thiourea with respect to $[\text{Ag(I)}]_{\text{tot}}$ was always present in the titrated solution to avoid formation of precipitate, so that the data refer to homogeneous equilibria and not to solubility-product-controlled reactions ($[\text{Tu}]_{\text{tot}}/[\text{Ag(I)}]_{\text{tot}} > 5$. For low thiourea concentrations, the upper limit of $[\text{Ag(I)}]_{\text{tot}}$, referred to below in the investigated concentration ranges, was suitably lowered).

The measuring cell can be represented as follows:

Ag	$[\text{AgNO}_3]_{\text{tot}} = \text{const.}$ $[\text{NaSCN}]_{\text{tot}} = \text{const.}$ $[\text{Thiourea}]_{\text{tot}} = \text{const.}$ $[\text{Halide}]_{\text{tot}} = \text{var.}$ $\mu = 1 \text{ for } \text{KNO}_3$	KNO_3 sat. salt bridge	Sat. calomel electrode
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Exhibit 1 refers to the investigated concentration ranges. Titrations were carried out for five different equally-spaced $[\text{Ag(I)}]_{\text{tot}}$ concentrations, six different $[\text{thiourea}]_{\text{tot}}$ concentrations and six different $[\text{SCN}^-]$ concentrations, i.e. $5 \times 6 \times 6 = 180$ titrations at different temperatures.

EXHIBIT 1. Concentration ranges

$2 \times 10^{-6} \text{ M}$	$\leq [\text{AgNO}_3]_{\text{tot}}$	$\leq 6 \times 10^{-6} \text{ M}$	(five concentrations)
0 M	$\leq [\text{NaSCN}]_{\text{tot}}$	$\leq 4 \times 10^{-2} \text{ M}$	(six concentrations)
$8 \times 10^{-6} \text{ M}$	$\leq [\text{Thiourea}]_{\text{tot}}$	$\leq 8 \times 10^{-4} \text{ M}$	(six concentrations)
0 M	$\leq [\text{KCl}]_{\text{tot}}$	$\leq 1.67 \times 10^{-1} \text{ M}$	(ten concentrations)
0 M	$\leq [\text{KBr}]_{\text{tot}}$	$\leq 1.07 \times 10^{-1} \text{ M}$	(ten concentrations)
0 M	$\leq [\text{KI}]_{\text{tot}}$	$\leq 1.67 \times 10^{-3} \text{ M}$	(ten concentrations)

The mathematical analysis of the experimental data was as described in our previous contributions [1–4] where details can be found; alternatively, details of the data processing can be obtained from the authors.

RESULTS AND DISCUSSION

Table 1 reports the complexive stability constants ($\log \beta_i$, β_i in $\text{mol}^{-i} \text{dm}^{3i}$) for the overall formation ($\text{Ag(I)} + m\text{Tu} + n\text{Tcy} + p\text{X} = \text{AgTu}_m\text{Tcy}_n\text{X}_p$) of the identified complexes. The two-ligand system $\text{Ag(I)}\text{-Tu-Tcy}$ is common to the investigated systems. The data for the single ligand (AgTu_m , AgTcy_n) and the thiourea–thiocyanate mixed ligand complexes ($\text{AgTu}_m\text{Tcy}_n$) come from different systems, as indicated in the S (System) column in Table 1.

Under the experimental conditions of this work, single ligand mono- and dicoordinated complexes with thiourea, thiocyanate or iodide have been identified; however, only monocoordinated complexes were identified for the other ligands (Cl^- , Br^-). Two- and three-ligand mixed complexes up to coordination level $N = 3$ are also present.

Enthalpy and entropy changes (kJ mol^{-1} and $\text{kJ mol}^{-1} \text{K}^{-1}$ respectively, Table 2) were deduced from the dependence of ΔG on temperature assuming a linear behaviour. They can be proposed as the most probable values within the investigated temperature range.

Thermodynamic data for two- and three-ligand halide–thiocyanate mixed complexes (designated * in Table 2) are published here for the first time. For the other complexes, literature thermodynamic data [1–3] were referred to the same experimental conditions as in this work. In these cases, the data of Table 1 together with those already reported have been used simultaneously for calculating the numbers in Table 2. When a number of ΔG values were available at a temperature, their average value was employed in the calculation.

Comparison with previous results

Compared with the results of earlier studies [1–5], lower coordinated complexes are found for the lower ligand concentrations used here. This is because highly reliable thermodynamic data are obtained for low coordinated substrata.

The formation constants (Table 2) are in fair agreement with those already reported [1,3], although $\log \beta_1$ and $\log \beta_2$ for the formation of AgTcy and AgTcy_2^- are lower in the present work.

For AgTcy_2^- , even a superficial inspection of the literature [6–8] reveals a scattered set of $\log \beta_2$ values. At $t = 25^\circ \text{C}$, $\log \beta_2$ values ranging from

TABLE 2

Most probable $\log \beta_n$ ($\text{mol}^{-n} \text{dm}^{3n}$), free energy, enthalpy and entropy changes (kJ mol^{-1} , kJ mol^{-1} and $\text{kJ mol}^{-1} \text{K}^{-1}$, respectively) for the overall complex formation $\text{Ag(I)}-\text{SCN}_2\text{H}_4-\text{SCN}^--\text{X}$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$) in aqueous solution at $t = 25^\circ \text{C}$ and ionic strength $\mu = 1$ for KNO_3

Formula	$\log \beta_n$	$-\Delta G$	ΔH	ΔS	I^a
AgTu^+	7.52	42.95	-60.12 ± 13	-57 ± 13	3
AgTu_2^+	10.32	58.8	-83.56 ± 6	-83 ± 19	3
AgTcy	5.67	32.36	-82.36 ± 11	-167 ± 38	3
AgTcy_2^-	7.44	42.48	-64.00 ± 16	-71 ± 44	3
AgTuTcy	9.09	51.88	-93.00 ± 8	-138 ± 26	3
AgTuTcy_2^-	10.89	62.15	-89.50 ± 12	-91 ± 40	3
AgTu_2Tcy	10.12	69.19	-134.0 ± 11	-216 ± 38	3
AgCl	4.20	23.98	-48.90 ± 1	-80 ± 4	3
AgTuCl	8.36	47.73	-47.10 ± 5	-2 ± 18	3
$\text{AgTcyCl}^- *$	6.12	34.93	-55.40 ± 22	-68 ± 76	0
$\text{AgTuTcyCl}^- *$	10.29	58.74	-43.50 ± 28	$+51 \pm 93$	0
$\text{AgTcy}_2\text{Cl}^{2-} *$	8.90	50.81	-15.00 ± 17	-216 ± 57	0
AgBr	6.42	36.63	-26.90 ± 29	$+32 \pm 98$	3
AgTuBr	9.26	52.87	-75.50 ± 32	-76 ± 109	3
AgTcyBr^-	7.05	40.24	-68.00 ± 77	-96 ± 265	0
$\text{AgTuTcyBr}^- *$	10.80	61.57	$-51.00 \pm 71?$	$+34 \pm 243$	0
$\text{AgTcy}_2\text{Br}^{2-} *$	9.11	52.02	-45.00 ± 56	$+23 \pm 194$	0
AgI	8.93	50.96	-44.00 ± 27	$+21 \pm 92$	3
AgI_2^-	12.72	72.58	-28.20 ± 19	$+149 \pm 64$	3
AgTuI	11.81	67.40	$-61.30 \pm 6??$	$+20 \pm 21$	0
AgTcyI^-	10.03	57.26	-69.00 ± 12	-42 ± 40	0
$\text{AgTcyTuI}^- *$	13.29	75.87	-47.00 ± 32	$+96 \pm 106$	0
$\text{AgTcy}_2\text{I}^{2-} *$	11.68	66.69	-36.00 ± 50	$+101 \pm 167$	0

^a The original data were smoothed by using I points before calculating the enthalpy and entropy changes.

7.57 to 10 are found. The value $\log \beta_2 = 7.44$, reported in Table 2, is consistent with the lowest value of the whole set.

For the homogeneous equilibrium $\text{Ag(I)} + \text{Tcy} = \text{AgTcy}$ (AgTcy in solution), one can only refer to the data in ref. 3 because the other literature data [6,7] concern the solid solution equilibrium $\text{Ag(I)} + \text{Tcy} = \text{AgTcy}_{\text{solid}}$, which is controlled by the solubility product. It is impossible to judge rigorously the validity of a particular value. Nevertheless, there are well founded reasons for considering the value $\log \beta_1 = 5.75$ to be reliable for AgTcy (Table 2). Firstly, the Tcy concentration range used here favours the formation of low coordinated $\text{Ag(I)}-\text{Tcy}$ complexes, more than do the concentrations previously investigated. Secondly, the value $\log \beta_1 = 5.76$ is more consistent than 7.77 [3] with the widely known analogy in the behaviours of SCN^- and Cl^- toward Ag(I) in aqueous solution at ordinary temperatures. Finally, a higher statistical reliance must be assigned to the

present value because it has been deduced, as previously mentioned, by taking into account a larger set of data, including values already published. This also holds for ΔH and ΔS , for which there is general agreement, in some cases, with the data already reported.

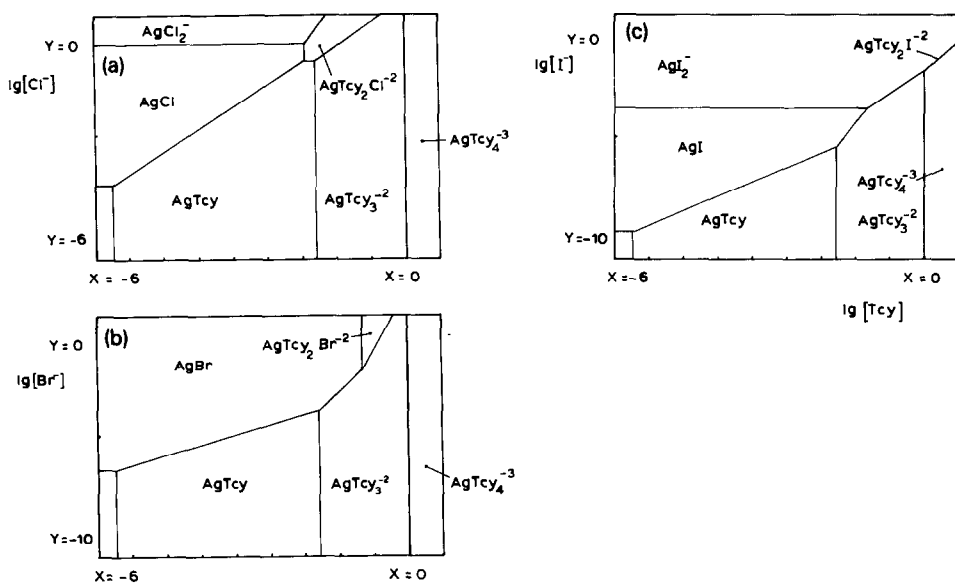


Fig. 1. Binary predominance diagrams for $\text{Ag(I)-SCN}^- - \text{X}$ ($\text{X} = \text{Cl}^-$, Br^- , I^-) complexes at ionic strength $\mu = 1$ for KNO_3 and $t = 25^\circ \text{C}$ in aqueous solution. The configurations used are the following:

Formula	System		
	(A) $\text{Ag(I)-SCN}^- - \text{Cl}^-$ $\log \beta$	(B) $\text{Ag(I)-SCN}^- - \text{Br}^-$ $\log \beta$	(C) $\text{Ag(I)-SCN}^- - \text{I}^-$ $\log \beta$
Ag(I)	0	0	0
AgTcy	5.67	5.67	5.67
AgTcy_2^-	7.44	7.44	7.44
AgTcy_3^{2-}	9.97	9.97	9.97
AgTcy_4^{2-}	10.59	10.59	10.59
AgCl	4.20	—	—
AgCl_2^-	4.88	—	—
AgTcyCl^-	6.12	—	—
$\text{AgTcy}_2\text{Cl}^{2-}$	8.9	—	—
AgBr	—	6.42	—
AgTcyBr^-	—	7.05	—
$\text{AgTcy}_2\text{Br}^{2-}$	—	9.11	—
AgI	—	—	8.93
AgI_2^-	—	—	12.72
AgTcyI^-	—	—	10.03
$\text{AgTcy}_2\text{I}^{2-}$	—	—	11.68

The following discussion is based on the data reported in Table 2.

Predominance diagrams

Figure 1 shows the predominance areas for the complexes in the two-ligand systems $\text{Ag(I)}-\text{Tcy}-\text{X}$ ($\text{X} = \text{Cl}^-$, Br^- , I^-), drawn with the configurations reported at the foot of the respective figures.

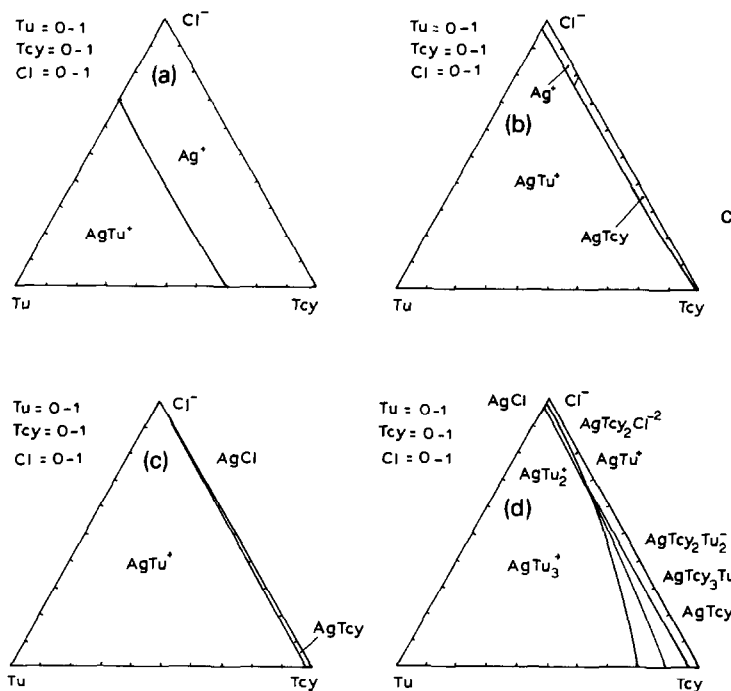


Fig. 2. Ternary predominance diagrams for $\text{Ag(I)}-\text{SCN}_2\text{H}_4-\text{SCN}^--\text{Cl}^-$ at ionic strength $\mu = 1$ for KNO_3 and $t = 25^\circ\text{C}$ in aqueous solution at different ligand concentrations: (a) $\Sigma[\text{L}]_{\text{free}} = 1 \times 10^{-7}$ M; (b) 1×10^{-5} M; (c) 1×10^{-3} M; and (d) 1×10^{-1} M. The sides of the triangle represent the parameter $[\text{L}_i]_{\text{free}} / \Sigma[\text{L}_i]_{\text{free}}$. The following configuration was used:

Formula	Log β	Formula	Log β
Ag(I)	0	AgTuTcy	9.09
AgTu^+	7.52	AgTuTcy_2^-	10.89
AgTu_2^+	10.32	AgTuTcy_3^{2-}	12.47
AgTu_3^+	12.87	AgTuCl	8.36
AgTcy	5.67	AgTuCl_2^-	9.67
AgTcy_2^-	7.44	AgTcyCl^-	6.12
AgTcy_3^{2-}	9.97	$\text{AgTcy}_2\text{Cl}^{2-}$	8.9
AgTcy_4^{2-}	10.59	AgTuTcyCl^-	10.29
AgCl	4.20	$\text{AgTu}_2\text{Tcy}^{2-}$	10.12
AgCl_2^-	4.88	$\text{AgTu}_2\text{Tcy}_3^{3-}$	13.35

For the systems Ag(I)–Tu–halide and Ag(I)–Tu–Tcy, the diagrams were practically coincident with those already published in ref. 1 and will not be reproduced here. In both two- and three-ligand systems, large predominance areas are found for single-ligand mono- and poly-coordinated complexes. There is no area pertaining to AgTcy_2^- , as it is always lower in percentage than the contiguous complexes. (Contiguous complexes are those differing from each other by one more or one less ligand.) In the binary Tu–halide diagrams, predominance areas are found for the three-

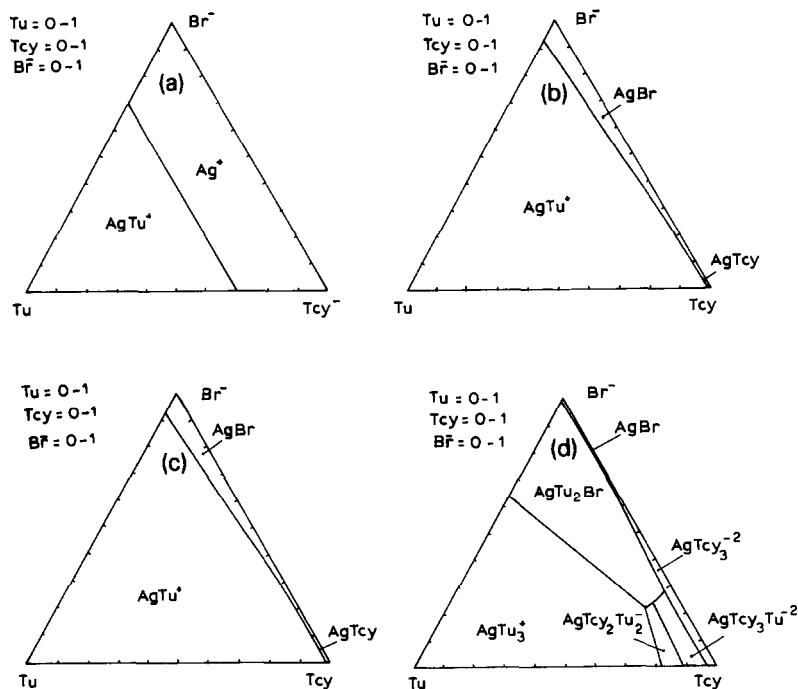


Fig. 3. Ternary predominance diagrams for Ag(I)–SCN₂H₄–SCN[−]–Br[−] at ionic strength $\mu = 1$ for KNO₃ and $t = 25^\circ\text{C}$ in aqueous solution at different ligand concentrations: (a) $\Sigma[\text{L}]_{\text{free}} = 1 \times 10^{-7}$ M; (b) 1×10^{-5} M; (c) 1×10^{-3} M; and (d) 1×10^{-1} M. The sides of the triangle represent the parameter $[\text{L}_i]_{\text{free}} / \Sigma[\text{L}_i]_{\text{free}}$. The following configuration was used:

Formula	Log β	Formula	Log β
Ag(I)	0	AgTuTcy	9.09
AgTu ⁺	7.52	AgTuTcy ₂ [−]	10.89
AgTu ₂ ⁺	10.32	AgTuTcy ₃ ^{2−}	12.47
AgTu ₃ ⁺	12.87	AgTuBr	9.26
AgTcy	5.67	AgTu ₂ Br	12.63
AgTcy ₂ [−]	7.44	AgTcyBr [−]	7.05
AgTcy ₃ ^{2−}	9.97	AgTcy ₂ Br ^{2−}	9.11
AgTcy ₄ ^{2−}	10.59	AgTuTcyBr [−]	10.80
AgBr	6.42	AgTu ₂ Tcy ^{2−}	10.12
		AgTu ₂ Tcy ₂ ^{3−}	13.35

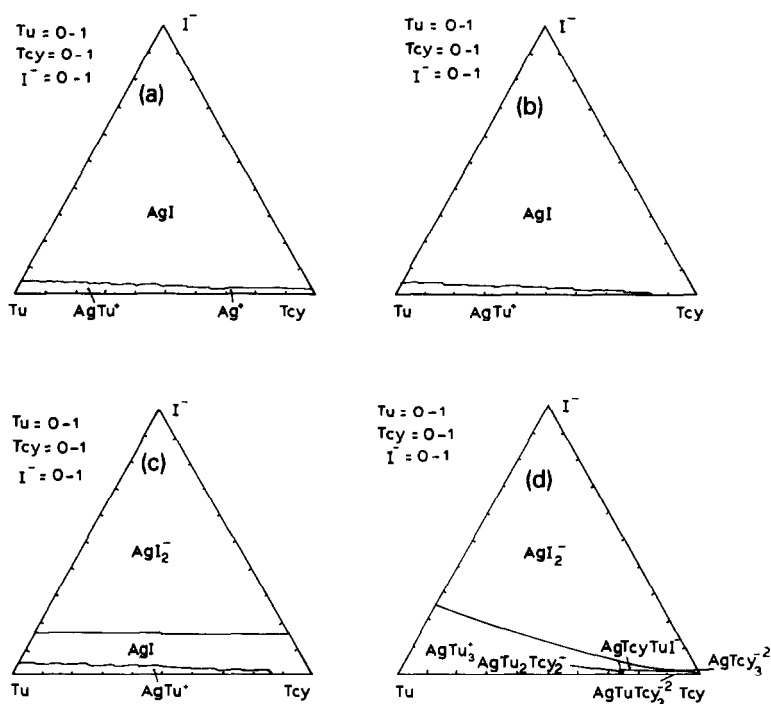


Fig. 4. Ternary predominance diagrams for $\text{Ag(I)}-\text{SCN}_2\text{H}_4-\text{SCN}^--\text{I}^-$ at ionic strength $\mu = 1$ for KNO_3 and $t = 25^\circ\text{C}$ in aqueous solution at different ligand concentrations: (a) $\Sigma[\text{L}]_{\text{free}} = 1 \times 10^{-7}$ M; (b) 1×10^{-5} M; (c) 1×10^{-3} M; and (d) 1×10^{-1} M. The sides of the triangle represent the parameter $[\text{L}_i]_{\text{free}}/\Sigma[\text{L}_i]_{\text{free}}$. The following configuration was used:

Formula	Log β	Formula	Log β
Ag(I)	0	AgTuTcy	9.09
AgTu^+	7.52	AgTuTcy_2^-	10.89
AgTu_2^+	10.32	AgTuTcy_3^{2-}	12.47
AgTu_3^+	12.87	AgTuI	11.81
AgTcy	5.67	AgTcyI^-	10.03
AgTcy_2^-	7.44	$\text{AgTcy}_2\text{I}^{2-}$	11.68
AgTcy_3^{2-}	9.97	AgTuTcyI^-	13.29
AgTcy_4^{3-}	10.59	$\text{AgTu}_2\text{Tcy}^{2-}$	10.12
AgI	8.93	$\text{AgTu}_2\text{Tcy}_2^{3-}$	13.35
AgI_2^-	12.72		

coordinated mixed complex $\text{AgTcy}_2\text{X}^{2-}$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$). Their importance decreases according to the sequence $\text{AgTcy}_2\text{Cl}^{2-} > \text{AgTcy}_2\text{Br}^{2-} > \text{AgTcy}_2\text{I}^{2-}$. In the last case, the surface is a very narrow strip.

The ternary diagrams in Figs. 2–4 refer to different ligand concentration levels ($\Sigma[\text{L}_i]_{\text{free}} = 1 \times 10^{-7}$ M (A), 1×10^{-5} M (B), 1×10^{-3} M (C), 1×10^{-1} M (D)). The parameters $[\text{L}_i]_{\text{free}}/\Sigma[\text{L}_i]_{\text{free}}$ are reported on the sides of the triangles (the free ligand molar fractions on the basis of the constant

sum of the free ligand concentrations; the sum remains constant in each diagram).

In the systems Ag(I)-Tu-Tcy-Cl^- and Ag(I)-Tu-Tcy-Br^- , Ag(I) is

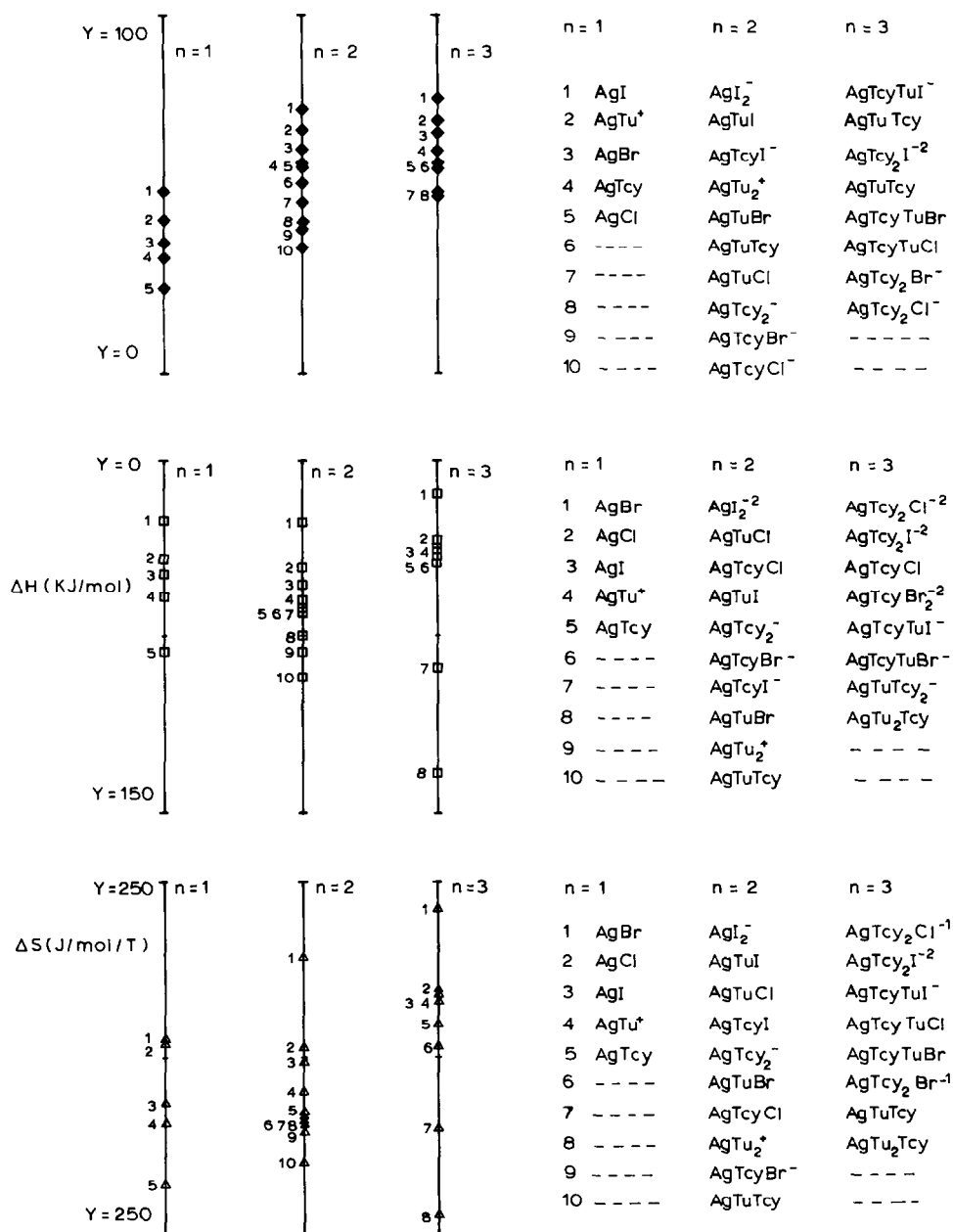


Fig. 5. Free energy, enthalpy and entropy changes for the overall Ag(I) complex formation $\text{Ag(I)} + n\text{Tu} + m\text{Tcy} + p\text{X} = \text{AgTu}_n\text{Tcy}_m\text{X}_p$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$) at $t = 25^\circ\text{C}$ and ionic strength $\mu = 1$ for KNO_3 in aqueous solution. Each line refers to a different coordination level.

essentially present as mono- or three-coordinated complexes with thiourea, depending on the various concentration levels of the free ligands. Mixed complexes with significant surfaces occur when $\sum[L_i]_{\text{free}} = 1 \times 10^{-1}$ M. They are $\text{AgTcy}_2\text{Tu}_2^-$, $\text{AgTcy}_3\text{Tu}^{2-}$ and $\text{AgTcy}_2\text{Br}^{2-}$. No predominance areas were found for AgTuTcyCl^- or AgTuTcyBr^- , nor for the mixed complexes Ag(I)-Tu-Cl^- .

In the ternary system Ag(I)-Tu-Tcy-I^- , Ag(I) occurs mainly as iodide complexes, but on increasing the ligand concentration level, formation of the three-coordinated AgTu_3^+ seems to be favoured. The areas pertinent to mixed complexes, significant in the systems Ag(I)-Tu-Tcy-Cl^- and Ag(I)-Tu-Tcy-Br^- , practically disappear in the system Ag(I)-Tu-1Tcy-I^- .

Free energy, enthalpy and entropy changes

All the deductions, relationships and implications related to the free energy changes refer to the data in Table 2, to 25°C and ionic strength $\mu = 1$. At different temperatures, the status can turn out to be different. In particular, on either side of the isoequilibrium temperatures, relationships of opposite order are obtained. Therefore, structural comments founded on free energies without due consideration of the experimental conditions and the metric units of the stability constants may be suspect.

Figure 5 shows the free energy, enthalpy and entropy changes for the overall complexing reactions. The vertical lines refer to different coordination levels, N (the total number of coordinated ligands). The free energy values are uniformly distributed in the range 20–40 kJ mol⁻¹: the reactions cannot be classified or grouped on this basis.

By means of the data in Table 2, two general reaction series can be established.

(i) The reactions between a specific substratum and different entering groups (one or more, simultaneously: $\text{Sub} + \text{X} = \text{Sub-X}$ or $\text{Sub} + \text{X} + \text{Y} + \dots = \text{Sub-X-Y}\dots$, where Sub is invariant and X and $\text{Y}\dots$ are varied).

(ii) The reactions between different substrata and the same entering group(s) ($\text{Sub} + \text{X} = \text{Sub-X}$ or $\text{Sub} + \text{X} + \text{Y} + \dots = \text{Sub-X-Y}\dots$ where Sub varies and X and $\text{Y}\dots$ are invariant).

In case (i), where X and Y vary, the various series give the affinity sequence of the entering groups as a function of the nature of the substratum. In case (ii), the affinity relationships of the substrata as a function of the entering group(s) are obtained.

For the affinities of Ag(I) towards single ligands (the series of reactions $\text{Ag(I)} + \text{X} = \text{AgX}$; $\text{X} = \text{variables}$), the sequence $\text{Cl}^- < \text{Tcy} \leq \text{Br}^- \leq \text{Tu} \leq \text{I}^-$ was obtained (Sequence (1)).

For coordination level $N = 2$ (the series of reactions $\text{Ag(I)} + \text{X} + \text{Y} = \text{AgXY}$; $\text{X}, \text{Y} = \text{variables}$), the stability order among pairs of ligands is given

by $(\text{Cl}^-, \text{Tcy}) \leq (\text{Tcy}, \text{Tcy}) \leq (\text{Tcy}, \text{Br}^-) \leq (\text{Cl}^-, \text{Tu}) \leq (\text{Tcy}, \text{Tu}) \leq (\text{Br}^-, \text{Tu}) \leq (\text{Tu}, \text{Tu}) \leq (\text{Tu}, \text{I}^-) \leq (\text{I}^-, \text{I}^-)$ (Sequence (2)).

For the reaction series $\text{Ag(I)} + \text{X} + \text{Y} + \text{Z} = \text{AgXYZ}$ (X, Y, Z = variables), the sequence $(\text{Cl}^-, \text{Tcy}, \text{Tcy}) \leq (\text{Br}^-, \text{Tcy}, \text{Tcy}) \leq (\text{Cl}^-, \text{Tcy}, \text{Tu}) \leq (\text{Br}^-, \text{Tcy}, \text{Tu}) \leq (\text{Tcy}^-, \text{Tcy}, \text{Tu}) \leq (\text{Tcy}^-, \text{Tcy}, \text{I}^-) \leq (\text{Tcy}^-, \text{Tu}, \text{Tu}) \leq (\text{Tcy}^-, \text{Tu}, \text{I}^-)$ was obtained (Sequence (3)).

In Sequences (1)–(3) the operator \leq holds only for terms directly connected by the operator. For groups far apart in the sequence (e.g. $(\text{Cl}^-, \text{Tcy})$ and $(\text{Br}^-, \text{Tcy})$ in Sequence (1)), the operator $<$ holds.

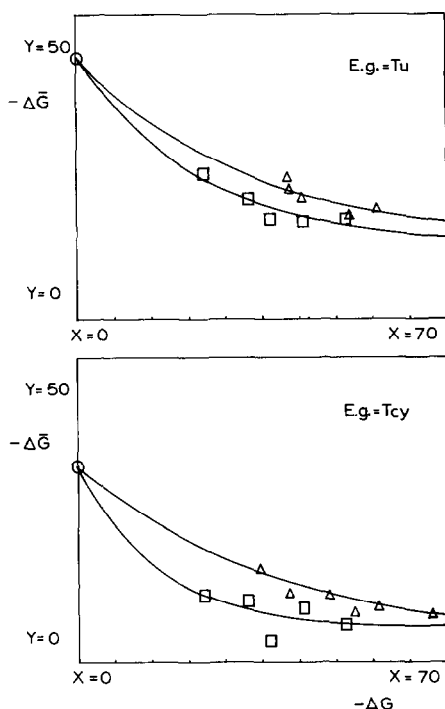


Fig. 6. Free energy relationships between the affinities towards the entering group and the overall thermodynamic stability of the reacting substrata in aqueous solution at $t = 25^\circ\text{C}$ and ionic strength $\mu = 1$ for KNO_3 ; \square , monocoordinated reacting substrata; Δ , dicoordinated reacting substrata; and (\circ) , Ag(I) . The full lines were drawn with the model $Y = A + B \exp(-CX)$. The parameters evaluated by non-linear least-squares fitting are:

		Entering group Tu	Entering group Tcy
Upper line	A	11.95 ± 4.8	3.16 ± 3.7
	B	31.02 ± 4.8	29.31 ± 3.7
	C	0.030 ± 0.01	0.027 ± 0.07
Lower line	A	11.48 ± 3.5	5.41 ± 4.0
	B	31.56 ± 3.6	27.00 ± 4.9
	C	0.43 ± 0.01	0.065 ± 0.04

TABLE 3

Most probable $\log K$ ($\text{mol}^{-1} \text{dm}^3$), free energy (kJ mol^{-1}), enthalpy (kJ mol^{-1}) and entropy changes ($\text{kJ mol}^{-1} \text{K}^{-1}$) for the stepwise complex formation $\text{Ag(I)-SCN}_2\text{H}_4\text{-SCN}^- \text{-X}$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$) in aqueous solution at $t = 25^\circ \text{C}$ and ionic strength $\mu = 1$ for KNO_3

Reaction	Log K	$-\Delta\bar{G}$	$\Delta\bar{H}$	$\Delta\bar{S}$
Entering group = Tcy				
$\text{Ag(I)} + \text{Tcy} = \text{AgTcy}$	5.67	32.36	-82.36	-167
Monocoord. sub.				
$\text{AgTcy} + \text{Tcy} = \text{AgTcy}^-$	1.77	10.12	+18.46	+96
$\text{AgCl} + \text{Tcy} = \text{AgClTcy}^-$	1.92	10.95	-6.5	+16
$\text{AgBr} + \text{Tcy} = \text{AgBrTcy}^-$	0.63	3.61	-41.1	-128
$\text{AgI} + \text{Tcy} = \text{AgITcy}^-$	1.10	6.30	-25.00	-63
$\text{AgTu}^+ + \text{Tcy} = \text{AgTuTcy}$	1.57	8.93	-32.9	-81
Dicoord. sub.				
$\text{AgTuCl} + \text{Tcy} = \text{AgTuClTcy}^-$	1.93	11.01	+3.6	+49
$\text{AgTuBr} + \text{Tcy} = \text{AgTuBrTcy}^-$	1.54	8.8	+23.79	+110
$\text{AgTuI} + \text{Tcy} = \text{AgTuITcy}^-$	1.48	8.47	+14.3	+76
$\text{AgTcyCl}^- + \text{Tcy} = \text{AgClTcy}_2^-$	2.78	15.88	+70	+291
$\text{AgTcyBr}^- + \text{Tcy} = \text{AgBrTcy}_2^-$	2.06	11.78	+23	+119
$\text{AgTcyI}^- + \text{Tcy} = \text{AgITcy}_2^-$	1.65	9.43	+33	+143
Entering group = Tu				
$\text{Ag(I)} + \text{Tu} = \text{AgTu}^+$	7.52	42.95	-60.12	-57
Monocoord. sub.				
$\text{AgTu}^+ + \text{Tu} = \text{AgTu}_2^+$	2.78	15.85	-23.44	-26
$\text{AgTcy} + \text{Tu} = \text{AgTcyTu}$	3.42	19.52	-10.6	+22
$\text{AgCl} + \text{Tu} = \text{AgClTu}$	4.16	23.75	+1.8	+86
$\text{AgBr} + \text{Tu} = \text{AgBrTu}$	2.84	16.24	-48.6	-108
$\text{AgI} + \text{Tu} = \text{AgITu}$	2.88	16.44	-17.3	-1
Dicoord. sub.				
$\text{AgTcy}_2^- + \text{Tu} = \text{AgTcy}_2\text{Tu}^-$	3.45	19.67	-25.5	-20
$\text{AgTcyTu} + \text{Tu} = \text{AgTcyTu}_2$	3.03	17.31	-41	-78
$\text{AgTcyCl}^- + \text{Tu} = \text{AgTcyClTu}^-$	4.17	23.54	+11.9	+112
$\text{AgTcyBr}^- + \text{Tu} = \text{AgTcyBrTu}^-$	3.75	21.43	+17	+130
$\text{AgTcyI}^- + \text{Tu} = \text{AgTcyITu}^-$	3.26	18.61	+22	-138
Entering group = Cl^-				
$\text{Ag(I)} + \text{Cl}^- = \text{AgCl}$	4.2	23.98	-48.9	-84
Monocoord. sub.				
$\text{AgTcy} + \text{Cl}^- = \text{AgTcyCl}^-$	0.45	2.03	+26.96	+99
$\text{AgTu}^+ + \text{Cl}^- = \text{AgTuCl}$	0.84	4.78	+13.12	+59
Dicoord. sub.				
$\text{AgTcy}_2^- + \text{Cl}^- = \text{AgTcy}_2\text{Cl}^{2-}$	1.46	8.33	+79	+294
$\text{AgTcyTu} + \text{Cl}^- = \text{AgTcyTuCl}^-$	1.20	6.86	+49.5	+189
Entering group = Br^-				
$\text{Ag(I)} + \text{Br}^- = \text{AgBr}$	6.42	36.63	-27	-32
Monocoord. sub.				
$\text{AgTcy} + \text{Br}^- = \text{AgTcyBr}^-$	1.38	7.88	+14.4	+71
$\text{AgTu}^+ + \text{Br}^- = \text{AgTuBr}$	1.74	9.92	-15.4	-20
Dicoord. sub.				
$\text{AgTcy}_2^- + \text{Br}^- = \text{AgTcy}_2\text{Br}^{2-}$	1.67	9.72	+19	+94
$\text{AgTcyTu} + \text{Br}^- = \text{AgTcyTuBr}^-$	1.71	9.79	+42	+172

TABLE 3 (continued)

Most probable $\log K$ ($\text{mol}^{-1} \text{dm}^3$), free energy (kJ mol^{-1}), enthalpy (kJ mol^{-1}) and entropy changes ($\text{kJ mol}^{-1} \text{K}^{-1}$) for the stepwise complex formation $\text{Ag(I)}-\text{SCN}_2\text{H}_4-\text{SCN}^--\text{X}$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$) in aqueous solution at $t = 25^\circ \text{C}$ and ionic strength $\mu = 1$ for KNO_3

Reaction	Log K	$\Delta\bar{G}$	$\Delta\bar{H}$	$\Delta\bar{S}$
Entering group = I^-				
$\text{Ag(I)} + \text{I}^- = \text{AgI}$	8.93	50.96	-44	+21
Monocoord. sub.				
$\text{AgI} + \text{I}^- = \text{AgI}_2^-$	3.79	21.62	+16	-1
$\text{AgTcy} + \text{I}^- = \text{AgTcyI}^-$	4.36	24.9	+13.4	+125
$\text{AgTu}^+ + \text{I}^- = \text{AgTuI}$	4.28	24.5	-1.2	+77
Dicoord. sub.				
$\text{AgTcy}_2^- + \text{I}^- = \text{AgTcu}_2\text{I}^{2-}$	4.24	24.21	+28	+172
$\text{AgTcyTu} + \text{I}^- = \text{AgTcyTuI}^-$	4.20	23.99	+46	+234

From these data and from data in a previous paper [1], Sequences (1) and (2) are identical when they refer to Ag(I) complex substrata (reaction series $\text{Sub} + \text{X} + \dots = \text{Sub-X} - \dots$: Sub , constant and X, \dots variable). The only exception arises in the series $\text{AgTcy}_2 + \text{X} = \text{AgTcy}_2\text{X}$ (AgTcy_2^- , constant and X variable) where Tcy exhibits much more affinity to AgTcy_2^- than to bromide ion ($\text{Br}^- \ll \text{Tcy}$).

In all the cases, the affinities lower systematically on increasing the overall thermodynamic stabilities of the reacting complexes. This principle characterises the free energy relationships of the other series of reactions founded on the interactions between the same entering group and variously coordinated substrata (Reaction: $\text{Sub} + \text{X} = \text{Sub-X}$, where Sub is variable, see Table 3). For $\text{X} = \text{halide}$, the number of reactions with the data in Table 3 is low. With $\text{X} = \text{Tcy}$ or Tu an asymptotic dependence of $\Delta\bar{G}$ for the coordination of single ligand on the overall thermodynamic stabilities of the reacting substrata (overall $\Delta\bar{G}$) is observed and an exponential behaviour is assumed. Of course the parameters of the calculated exponential regression must be improved with more data (see Fig. 6). In spite of this, for both entering groups (Tcy or Tu) higher affinities are systematically found toward the dicoordinated Ag(I) substrata than toward the monocoordinated ones.

The stepwise free energy changes (Table 3 and Fig. 7) show a sharp break between solvated Ag(I) and its complex substrata, independent of both the nature and number of the entering or coordinated ligands. Following the coordination of one or more ligands, Ag(I) is stabilised and the relationship $\Delta\bar{G}_1 \ll \Delta\bar{G}_{n>1}$ becomes a general feature of Ag(I) in aqueous solution at 25°C .

Moreover, the diagram in Fig. 7 proves that, under the experimental conditions of the present work, hydrated Ag(I) in aqueous solution is

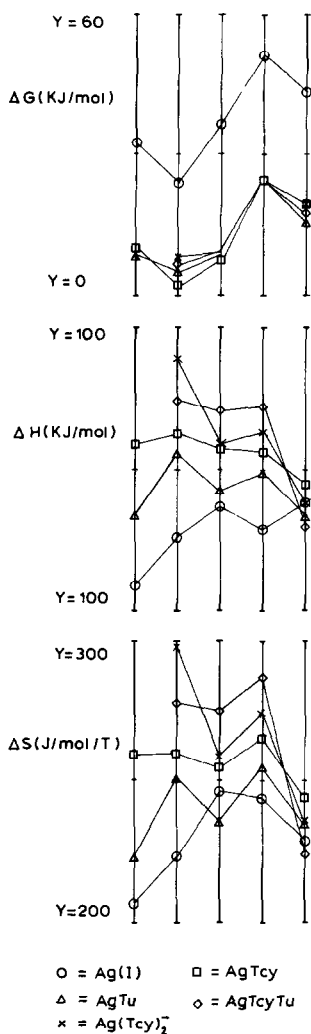


Fig. 7. Selected free energy, enthalpy and entropy changes for the stepwise complex formation $\text{Sub} + \text{X} = \text{Sub-X}$ (Sub = Ag(I) substrata) in aqueous solution at 25°C and $\mu = 1$ for KNO_3 . The different lines refer to different entering groups: ○, Ag(I); □, AgTcy; △, AgTu; ×, $\text{Ag}(\text{Tcy})_2^-$; and ◇, AgTcyTu.

stabilised by ligand coordination, independent (to a first approximation) of the nature of its coordination environment.

All the overall complexing reactions $\text{Ag(I)} + \text{X} + \text{Y} + \dots = \text{AgXY}\dots$ are exothermal but their ΔS values range from negative to positive. Their interval increases with complexive coordination level. The formation of monocoordinated AgBr and AgI shows almost the same susceptibilities to temperature change ($\Delta S = +32$ and $+21 \text{ kJ mol}^{-1} \text{ K}^{-1}$, respectively), totally different from the entropy changes for the formation of AgCl ($\Delta S = -48.4 \text{ kJ mol}^{-1} \text{ K}^{-1}$). With an overall complexive coordination level

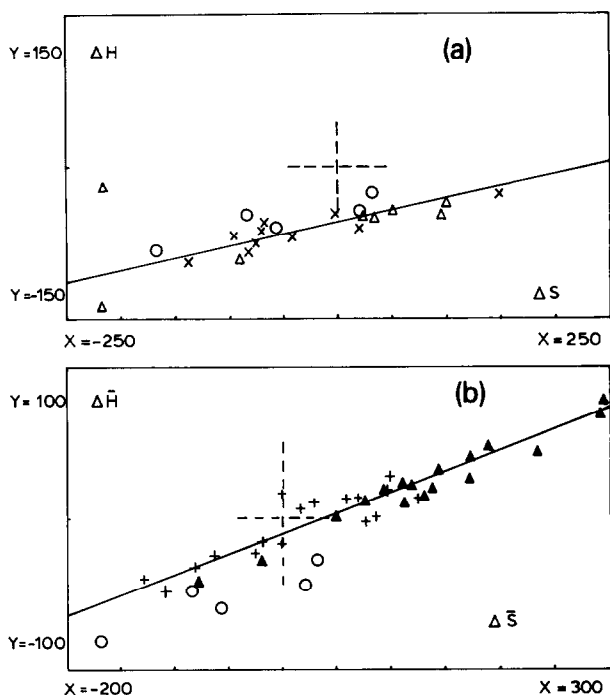


Fig. 8. Enthalpy-entropy change interdependence in Ag(I) overall (a) and stepwise (b) complex formation in aqueous solution at ionic strength $\mu=1$ for KNO_3 . (a), $\Delta H = -53.41(4.87) + 0.156(0.05)\Delta S$, $R = 0.585$ (isoequilibrium temp., $T_{\text{iso}} = 189$ K). (b), $\Delta \bar{H} = -10.22(1.85) + 0.276(0.01)\Delta \bar{S}$, $R = 0.957$ (isoequilibrium temp., $T_{\text{iso}} = 276$ K). Standard deviations are reported in parentheses. \circ , $\text{Ag(I)} + \text{L} = \text{AgL}$; \times , $\text{Ag} + \text{L} + \text{L}' = \text{AgLL}'$; \blacktriangle , $\text{AgL} + \text{L}' = \text{AgLL}'$; \triangle , $\text{Ag} + \text{L} + \text{L}' + \text{L}'' = \text{AgLL}'\text{L}''$; $+$, $\text{AgLL}' + \text{L}'' = \text{AgLL}'\text{L}''$.

N of 2 or 3, the relationship among the ΔS values is less clear, but in general, formation of complexes involving I^- (Tcy) remains the most favourable (unfavourable).

The pattern for the stepwise enthalpy or entropy changes (reactions $\text{Sub} + \text{X} = \text{Sub-X}$) is fairly different from that of the free energy changes. $\Delta \bar{H}$ and $\Delta \bar{S}$ are differently spread over their respective coordinates (each referring to a different entering group). The coordination of the first ligand is always the most enthalpically favoured (entropically disfavoured) and both the enthalpy and the entropy changes tend to become more positive on increasing the complexive coordination level of the substratum.

The changes in the thermodynamic parameters for the overall and stepwise complexation are correlated to some extent. Figure 8 shows the enthalpy changes plotted against the corresponding entropy changes. It is unnecessary to reproduce the other pairs of variables (ΔG versus ΔH and ΔG versus ΔS , or vice versa). In fact the occurrence of a relationship (correlation) between any two of three linearly related parameters (the

parameters of the Gibbs equation) implies automatically the occurrence of relationships (correlations) between the other pairs of parameters.

The overall and stepwise complex formations show different susceptibilities and, consequently, different isoequilibrium temperatures for the different ways in which the enthalpy–entropy interconnections originate.

In the diagram for the stepwise changes, the points for the formation of the monocoordinates AgX ($\text{X} = \text{Cl}^-$, Br^- , I^- , Tcy) lie on a more favourable position with respect to the line of the trend calculated using the data for the second and third stepwise coordination only. Moreover, there is no clear enthalpy (entropy) discrimination in the overall complexation in dependence of the coordination level. The $\Delta\bar{H}$ ($\Delta\bar{S}$) stepwise data show that the $\Delta\bar{H}$ ($\Delta\bar{S}$) values pass through a maximum corresponding to monocoordinates reacting substrata.

CONCLUSIONS

From the results obtained so far, it is possible to draw some conclusions concerning the formation of two-ligand mixed complexes. First, it is necessary to distinguish two general situations:

(a) When each of the two ligands (X or Y) forms complexes with the central ion that have very different stabilities, e.g. $\text{S}_2\text{O}_3^{2-}$ or Cl^- with Ag(I) . In such cases, the formation of single-ligand complexes prevails. When the metal ion is present as the complexed form MX_m , the addition of a second ligand Y in the system tends to induce the displacing reaction $\text{MX}_m + p\text{Y} = \text{MY}_p + m\text{X}$, depending on the experimental conditions.

(b) When each one of the two ligands (X or Y) forms complexes with comparable stabilities, e.g. the pairs Tcy– Cl^- or Ts– I^- with Ag(I) . In this case three different situations must be distinguished.

(i) X and Y exhibit low affinities towards the acceptor.

(ii) X and Y exhibit medium affinities towards the acceptor.

(iii) X and Y exhibit high affinities towards the acceptor.

Cases (i) and (iii) result in the same situations as in case (a): the predominance diagrams show areas for single-ligand complexes variously coordinated with one or the other ligand.

In case (ii), the areas for the mixed complexes assume higher significance.

Of course, the above classification is qualitative and needs to be refined (if possible) using quantitative criteria. Despite this, the conditions for the formation of mixed complexes in significant amounts are clearly identified.

Any attempt to assign quantitative definitions must take into account the fact that there is no sharp break between the various situations.

In the present case, the substratum-to-ligand affinity, the mutual property of the two reacting entities in the particular system in which they are considered, cannot be rationalised in terms of the electric charges (or

exclusively in terms of the electric charges) of the substratum and the ligand, either separately or together. This is demonstrated without any doubt by the affinity sequences found here and previously. In all cases, the $\Delta\bar{G}$ values do not follow a monotonous behaviour with the formal ionic charge of the variable terms of the series. Thus these results confirm that the electric charges do not represent the main factor in complex formation in water solution and that other factors, capable of reversing an order relationship, are present. In general, the substratum-to-ligand affinities (in the absence of steric hindrances) depend on the thermodynamic stabilities of both the substratum and the entering ligand.

In the exponential free energy relationships referred to in the literature [5,9], it is shown that in the coordination of Tcy or Tu, their affinities towards dicoordinated substrata ($X\text{-Ag-Y} + Z = \text{AgXYZ}$, $Z = \text{Tcy or Tu}$) are systematically greater than their affinities towards monocoordinated substrata ($\text{AgX} + Z = \text{AgXZ}$, $Z = \text{Tcy or Tu}$). Being dicoordinated complexes, more stable systematically than monocoordinates, the phenomenon is plainly in contrast with the above sentence regarding the dependence of the substratum-to-ligand affinities on the thermodynamic stabilities of the substratum itself. Furthermore, the phenomenon is also in contrast with the widely recognised relationship $\Delta\bar{G}_{n-1} < \Delta\bar{G}_n$. The behaviour illustrated in Fig. 6 indicates that in the single-ligand coordination ($\text{Sub} + X = \text{Sub-X}$), the mono- and dicoordinated Ag(I) complexes form two distinguished classes. In this way, the discrepancy between the above sentence and the present behaviour disappears because the statement must be considered within the class and not as a relationship between classes.

The substratum-to-ligand affinity decreases on increasing the complexive coordination level of the substrata; although found frequently, this is not to be considered an almost general rule for two reasons. Firstly the complexing reactions in solution occur between coordinatively saturated reagents (for the coordinated solvent molecules). Therefore, it is improper to speak of successive coordinations; it is more appropriate to consider successive reciprocal substitutions in the coordinatively saturated coordination spheres of the substratum and the ligand. Secondly, for most cases the two coordination reactions (the stepwise formation of the n th and $(n+1)$ th complexes) differ in their entropy changes; therefore they have different ΔG susceptibilities to temperature and there is an isoequilibrium point in the $\Delta G-T$ space which is an inversion point for the affinity relationships.

The cumulative and stepwise complexation reactions ($\text{Ag(I)} + nX + mY + pZ = \text{AgX}_n\text{Y}_m\text{Z}_p$ and $\text{Sub} + X = \text{Sub-X}$ respectively) show different compensative enthalpy-entropy effects (positive interdependence between ΔH and ΔS). The first series is characterised by lower $\Delta H-\Delta S$ susceptibilities and more negative ΔH_{res} .

In the stepwise complexation, the formation of AgX monocoordinates distinguishes for more favourable ΔH and ΔS values with respect to the

trend defined by the subsequent complexation. The point distribution underlines the fact that the solvent medium plays the greatest quantitative role in the second coordination reactions $\text{AgX} + \text{Y} = \text{AgXY}$.

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